ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM (EMSP) SYMPOSIUM

(Cosponsored with the Division of Analytical Chemistry)
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Characterization, Fate, and Transport of Subsurface Contamination (Organics, Metals, and Rads)

DIVISION OF ENVIRONMENTAL CHEMISTRY
225th American Chemical Society Meeting
New Orleans, LA
Thursday, March 27, 2003

Organizer: **T. Zachry**

Presiding: **L. McCoy**

Time	**Paper**
8:30 a.m.	Introductory Remarks.
8:40 a.m.	**Compositional effects on interfacial properties in contaminated systems: Implications for organic liquid migration and recovery.** L.M. Abriola, A.H. Demond, T.J. Phelan, D.M. O'Carroll, H.-L. Hsu and J.L. Ryder
9:05 a.m.	**Coupled hydrological and geochemical processes governing the fate and transport of radionuclides and toxic metals in the Hanford vadose zone.** P.M. Jardine, M.A. Mayes, S. Fendorf, M.N. Pace, X. Yin, J.M. Zachara and T.L. Mehlhorn
9:30 a.m.	**Using nonlinear dynamics for environmental management of the vadose zone and groundwater.** B. Faybishenko
9:55 a.m.	Intermission.
10:20 a.m.	**Noninvasive contaminant site characterization using geophysical induced polarization.** F.D. Morgan, J. Sogade, D. Lesmes, D. Coles, Y. Vichabian, F. Scira-Scappuzzo, W. Shi, A. Vandiver and W. Rodi
10:45 a.m.	**Development of accurate chemical equilibrium models for the Hanford waste tanks: New thermodynamic measurements and model applications.** A.R. Felmy, M.J. Mason, O.S. Qafoku, Y. Xia, Z. Wang and G. MacLean

11:10 a.m. **Evolution of REDOX tank waste plumes in Hanford vadose zone: A conceptual model developed through reactive transport studies.** J. Wan, T.K. Tokunaga, J.T. Larsen and Z. Zheng

11:35 a.m. **Microbially-mediated subsurface calcite precipitation for removal of hazardous divalent cations.** F.S. Colwell, R.W. Smith, F.G. Ferris, J.C. Ingram, A.-L. Reysenbach, Y. Fujita, T.L. Tyler, J.L. Taylor, A. Banta, M.E. Delwiche, T. McLing, M.M. Cortez and M.E. Watwood

12:00 p.m. Concluding Remarks.

ABSTRACTS

Compositional effects on interfacial properties in contaminated systems: Implications for organic liquid migration and recovery. Linda M. Abriola, Avery H. Demond, Thomas J. Phelan, Denis M. O'Carroll, Hsin-Lan Hsu and Jodi L. Ryder; Department of Civil & Environmental Engineering, The University of Michigan, 116 EWRE, 1351 Beal Ave, Ann Arbor, MI 48109-2125, Fax: 734-763-2275, abriola@engin.umich.edu.

An understanding of the transport behavior of dense non-aqueous phase organic liquids (DNAPLs) is a prerequisite for the accurate assessment of chemical exposure and the design of effective subsurface remediation strategies. This paper highlights results of an ongoing EMSP research project designed to explore the influence of solid and organic phase composition on DNAPL migration, entrapment and recovery from contaminated aquifers. The integrated research program includes small-scale laboratory investigations to examine the dependence of organic contaminant constitutive relationships (*e.g.*, capillary pressure-saturation, relative permeability, residual saturation and interphase mass transfer rates) on interfacial properties. Models developed from these observations are being incorporated into a compositional multiphase simulator to facilitate prediction of DNAPL behavior under conditions representative of field sites. Two-dimensional sand box experiments are also being undertaken to validate the modeling approach. Results from this research demonstrate the dramatic influence of interfacial property variation on DNAPL migration and retention.

Coupled hydrological and geochemical processes governing the fate and transport of radionuclides and toxic metals in the Hanford vadose zone. Philip M. Jardine[1], Melanie A. Mayes[1], Scott Fendorf[2], Molly N. Pace[1], Xiangping Yin[1], John M. Zachara[3] and Tonia L. Mehlhorn[1]; [1]Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6038, Oak Ridge, TN 37831, Fax: 865-576-8646, jardinepm@ornl.gov, mayesma@ornl.gov; [2]Dept. of Geological and Environmental Sciences, Stanford University; [3]Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory.

At the D.O.E. Hanford Reservation, accelerated migration of radionuclides has been observed in the vadose zone underlying the tank farms. Our goal is to provide an improved understanding and predictive capability of the coupled hydrogeochemical mechanisms responsible for observed migration. Our approach is to perform a suite of experiments ranging from novel surface interrogation techniques (*e.g*., XAS) to miscible displacement experiments on disturbed and undisturbed sediments from the Hanford, Plio-Pleistocene and Ringold formations. Results indicate during unsaturated conditions hydrologic processes governing transport are a strong function of sediment layering in the Hanford and Ringold formations. The transport of radionuclides and toxic metals (U, Cr(VI), Cs, Sr and Co) is influenced by reactive geochemical nonequilibrium, sedimentary mineralogy and solution chemistry. This research will provide new insights into how physical and mineralogical heterogeneities (*e.g*. stratification, pore regime connectivity, mineral composition along flowpaths) influence contaminant retardation and degree of geochemical nonequilibrium during transport.

Using nonlinear dynamics for environmental management of the vadose zone and groundwater. Boris Faybishenko; Earth Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, Fax: 510-486-5686, BAFaybishenko@lbl.gov.

The need to improve characterization and prediction methods for flow and transport in partially saturated and saturated heterogeneous soils and fractured rock has long been recognized. Such improvement would be specifically welcomed in the fields of environmental management, containment and remediation of contaminated sites. Until recently, flow and transport processes in heterogeneous soils and fractured rock (with oscillating irregularities) were assumed to be random and were analyzed using conventional stochastic and deterministic methods. In this presentation, I will present the results of laboratory and field investigations of flow and transport in unsaturated soils and fractured rock, applying the methods of nonlinear dynamics and deterministic chaos. I will discuss using these methods for the development of improved characterization and prediction methods as well as for the development of remediation technologies for contaminated soils and groundwater.

Noninvasive contaminant site characterization using geophysical induced polarization. F. D. Morgan[1], J. Sogade[1], D. Lesmes[2], D. Coles[1], Y. Vichabian[1], F. Scira-Scappuzzo[1], W. Shi[1], A. Vandiver[1] and W. Rodi[1]; [1]Earth Resources Laboratory, Dept. of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, morgan@erl.mit.edu; [2]Department of Geology and Geophysics, Boston College.

Results of aspects of a broad foundational study of time domain IP (TDIP) and spectral IP (SIP) for contaminant site characterization are presented. This ongoing study encompassed laboratory studies of coupled effects of rock/soil microgeometry and contaminant chemistry on induced polarization (IP), an investigation of electromagnetic coupling (EMC) noise and development of 3D modeling and inversion codes. SIP requires extensions to higher frequencies (above the typical 100Hz threshold) and EMC becomes the major limitation for field implementation, because conventional correction methods are inadequate at required higher frequencies. A proposed methodology is outlined, based on a model of all EMC components, that addresses the EMC problem by coupling IP and electromagnetic induction in modeling and inversion. Examples of application of IP and SIP to contaminant mapping and detection for TDIP and SIP will be presented for FS-12 plume at Massachusetts Military Reservation and a suspected DNAPL plume at Savannah River Site.

Development of accurate chemical equilibrium models for the Hanford waste tanks: New thermodynamic measurements and model applications. Andrew R. Felmy[1], Marvin J. Mason[1], Odeta S. Qafoku[2], Yuanxian Xia[3], Zheming Wang[1] and Graham MacLean[4]; [1]Environmental Dynamics and Simulation, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, ar.felmy@pnl.gov; [2]William R. Willey Laboratory, Pacific Northwest National Laboratory; [3]Actinide and Trace Metal [4]Fluor Federal Services.

Developing accurate thermodynamic models for predicting the chemistry of the high-level waste tanks at Hanford is an extremely daunting challenge in electrolyte and radionuclide chemistry. These challenges stem from the extremely high ionic strength of the tank waste supernatants, presence of chelating agents in selected tanks, wide temperature range in processing conditions and the presence of important actinide species in multiple oxidation states. This presentation summarizes progress made to date in developing accurate models for these tank waste solutions, how these data are being used at Hanford and the important challenges that remain. New thermodynamic measurements on Sr and actinide complexation with specific chelating agents (EDTA, HEDTA and gluconate) will also be presented.

Evolution of REDOX tank waste plumes in Hanford vadose zone: A conceptual model developed through reactive transport studies. Jiamin Wan, Tetsu K. Tokunaga, Joern T. Larsen and Zuoping Zheng; Earth Science Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720, Fax: 510-486-7797, jmwan@lbl.gov.

Decisions on remedial actions for leakage of highly radioactive tank waste solutions at the Hanford Site will depend highly on understanding of the current distribution and future migration of contaminants in the subsurface. The geochemical data obtained from borehole drilling at SX tank farm in the 200 Area, by Tank Farm Vadose Zone Characterization Project of the U.S. Department of Energy, revealed valuable insights as well as some results that challenge our basic understanding of waste plume evolution. In response to these needs and challenges, we have been investigating reactive transport of tank waste solutions in Hanford sediments through laboratory column experiments combined with geochemical modeling. Analyses of solid and aqueous phases within different zones of contaminant plumes, along with thermodynamic predictions provide the basis for our conceptual model. This model reveals the primary processes controlling evolution of REDOX waste plumes in the Hanford vadose zone.

Microbially-mediated subsurface calcite precipitation for removal of hazardous divalent cations. Frederick S. Colwell[1], R. W. Smith[2], F. Grant Ferris[3], Jani C. Ingram[4], A.-L. Reysenbach[5], Yoshiko Fujita[1], T. L. Tyler[6], J. L. Taylor[6], A. Banta[5], M. E. Delwiche[1], T. McLing[7], Marnie M. Cortez[4] and M. E. Watwood[8]; [1]Biotechnologies Department, Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2203, Fax: 208-526-0828, fxc@inel.gov; [2]University of Idaho; [3]Department of Geology, University of Toronto; [4]Chemistry Department, Idaho National Engineering and Environmental Laboratory; [5]Portland State University; [6]Idaho National Engineering and Environmental Laboratory; Idaho State University; [7]Geosciences Department, Idaho National Engineering and Environmental Laboratory; [8]Idaho State University.

We are investigating microbially-mediated acceleration of calcite precipitation and co-precipitation of hazardous divalent cations (*e.g.*, ^{90}Sr) in calcite saturated subsurface systems. In theory, the addition of urea to an aquifer or vadose zone and its subsequent hydrolysis by indigenous microbes will cause an increase in alkalinity, pH and calcite precipitation. Lab studies indicated the ability of various bacteria to precipitate calcite through urea hydrolysis and that incorporation of strontium in biogenically-formed calcite is greater than in abiotically formed calcite. Results from a field experiment in a pristine location in the Snake River Plain aquifer involving the phased addition of molasses and then urea showed increases in total cell numbers, rate of urea hydrolysis and calcite formation during the study. The combined diagnostic approaches of microbiology, molecular ecology and analytical chemistry demonstrate the feasibility of this biogeochemical manipulation for subsurface remediation at arid Western DOE sites such as Hanford and INEEL.